more of the dilute nitric acid being added, if the color is not completely discharged after ten or fifteen minutes' boiling. A minute or two after the color has completely disappeared the solution is taken from the flame, cooled and neutralized with sodium carbonate. To secure exact neutralization, a little calcium carbonate may be added at first and then sodium carbonate solution until a precipitate just forms. The chlorine is then determined by titration with standard silver nitrate, using potassium chromate as indicator.

The results of twelve analyses of mixtures of potassium iodide, potassium bromide and sodium chloride are tabulated below. It will be observed that, with two exceptions, the differences between the taken and found quantities of potassium iodide and sodium chloride do not exceed 0.3 milligram.

ON CEROPTENE, A NEW ORGANIC COMPOUND.

BY W. C. BLASDALE.

Received August 21, 1903.

IN AN article published[1] in 1893 the writer briefly described an organic compound which had been obtained from the fronds of *Gymnogramme triangularis,* for which the name *ceroptene* was provisionally proposed. It was shown in that paper that this compound, together with others of unknown composition, was secreted by peculiar gland-tipped hairs, which were found in great abundance on the under surfaces of the fronds of the beforementioned plant. The yellow secretion is produced in such abundance as to completely envelop and conceal the dorsal surfaces of the fully developed fronds, whence the popular name of the plant, the "golden-back" fern.

Secretions of a somewhat similar character are produced by other species of ferns, especially certain groups of species belonging to the genera *Gymnogramme, Cheilanthes* and *Nothol-oena;* possibly, also the secretions produced by certain species of *Primula* are of a like nature. Though none of these secretions appear to have been submitted to a chemical investigation, the opinion expressed or implied in most of the botanical treatises, which deal with these plants is that they consist of wax. Goep-

---

[1] *Erythea* (botanical journal published at Berkeley from 1893 to 1899), 1, 252.

pert,[1] however, considered them to be of a resinous nature, though his only reason for doing so is their solubility in alcohol. Klotzsch[2] has also described a crystalline compound which he obtained accidentally by dissolving the indument from the fronds of various species of *Gymnogramme* with alcohol and allowing the solution to evaporate spontaneously. This substance melted at 50°, was soluble in hot water, and in the opinion of this investigator was a "pseudo-stearoptene," that is, a compound related to coumarine, an opinion for which very little evidence was offered.

Though the golden-back fern is a comparatively common species on the Pacific coast, the amount of secretion yielded by it is but small, and it has been a difficult matter to secure the large quantities necessary for the investigation. The work has been further hindered because many of the compounds obtained were of a tarry nature and could not be purified when working on the small amounts available. Inasmuch as a large number of facts regarding the properties of the compound ceroptene have been gradually acquired it has seemed advisable to publish these at the present time, even though final conclusions regarding its structural formula can not be offered.

PREPARATION OF CEROPTENE.

Experiments with a variety of solvents showed that the entire secretion is easily soluble in either benzene or petroleum-ether, more readily, however, in the former solvent. The dried fronds, exclusive of stems, were treated in an extraction apparatus with either one of these solvents till complete solution of the indument had been effected, the solution thus obtained filtered from spores, etc., the excess of solvent distilled off, and the residual solution allowed to evaporate. In time there appeared wart-like groups of platy crystals, together with a much larger amount of a yellow amorphous substance, the total yield ranging from 4.4 to 6.4 per cent. Repeated crystallization of the crystalline portion from either benzene, ethyl ether, or alcohol finally gave a compound which melted very sharply at 135°. This is the compound to which the name ceroptene has been given; it constitutes about one-third of the total secretion. The non-crystalline portion melts

---

[1] "*Actorum Academiæ Caesareæ Leopoldino-Carolinæ Naturæ Curiosorum*," **18**, Suppl. I, page 229.

[2] *J. prakt. Chem.*, **55**, 242.

at about 58° and is evidently a mixture of several substances, of which the only one identified with certainty is cerotic acid. Various methods of treating this portion were used; the most satisfactory was to digest with a dilute aqueous solution of potassium hydroxide, in which the cerotic acid is but slowly soluble, while the other constituents of the secretion dissolve almost immediately. The insoluble cerotic acid was purified by repeated treatment with hot alcohol. The alkaline solution was acidified, which reprecipitated the tarry substance held in solution, and the precipitate thus produced treated with a small amount of cold alcohol. This treatment left insoluble a further quantity of ceroptene and a very minute quantity of a second crystalline substance. Thus far but little progress has been made in the separation of the tarry products dissolved by the alcohol.

DESCRIPTION OF CEROPTENE.

The pure substance forms beautiful tabular or prismatic crystals of a sulphur-yellow color. It is readily dissolved by acetone, chloroform, carbon bisulphide, carbon tetrachloride, and less readily by ether. It is readily soluble in alcohol or benzene, but the solubility is greatly increased by a slight increase in the temperature of these solvents. Concentrated sulphuric, hydrochloric, or acetic acids readily dissolve ceroptene and it may be recovered from the two latter solvents by spontaneous evaporation. Dilution of all of the three acid solutions produces a light yellow precipitate, which on treatment with benzene yields the original ceroptene. With the sulphuric acid solution, however, the precipitation takes place very slowly and small amounts of tarry substances are produced at the same time. On heating, it fuses with the formation of a clear lemon-yellow liquid but, as the temperature is increased, decomposes with the formation of volatile compounds, which have a strong aromatic odor. By transmitted light, the crystals are of a clear lemon-yellow color, but by reflected light they show a pronounced green fluorescence. The alcoholic solution also shows the latter phenomena to a slight degree. Neither the crystals nor their solutions rotate the plane of polarized light. The specific gravity of the crystals at a temperature of 15°, compared with water at the same temperature, is 1.1976.

CRYSTALLOGRAPHY OF CEROPTENE.

Crystallization from different solvents produced individuals showing a considerable diversity of habit, though the number of distinct crystal forms concerned was not great. The best were obtained from benzene, from which solvent perfect individuals of flat, tabular form sometimes 2 cm. in length and 3 mm. in thickness could be obtained; chloroform or glacial acetic acid gave less perfect forms; alcohol usually gave needle-shaped or prismatic forms of smaller size. Examination of the crystals with polarized light in a direction at right angle to the plane of greatest development showed the emergence of an optic axis, the latter placed very eccentrically. This fact, as well as the symmetry of the crystal form, clearly classes them as triclinic. The plane of greatest development was, therefore, chosen as the base and the two planes showing the least inclination to it, as brachy- and macropinacoids; it was then easy to refer the remaining planes to either dome or prismatic faces. Although the crystals were well formed, many of the faces, especially the macropinacoid, failed to give good reflections owing to the curvatures or other imperfections. The accompanying table gives the results of the measurements of the principal interfacial angles.

MEASUREMENTS IN THE BRACHY ZONE.

Angle $(001) \wedge (010)$. Average of seven measurements, 67° 29′.
Angle $(0\bar{1}0) \wedge (0\bar{1}1)$. Average of two measurements, 55° 59′.
Angle $(001) \wedge (0\bar{1}1)$. Average of three measurements, 56° 57′.
Angle $(001) \wedge (011)$. Result of one measurement, 33° 39′.

MEASUREMENTS IN THE MACRO ZONE.

Angle $(001) \wedge (100)$. Average of four measurements, 85° 45′.
Angle $(\bar{1}00) \wedge (\bar{1}01)$. Average of two measurements, 42° 52′.
Angle $(001) \wedge (\bar{1}01)$. Average of eight measurements, 50° 49′.

MEASUREMENTS IN THE VERTICAL ZONE.

Angle $(100) \wedge (010)$. Average of five measurements, 84° 11′.
Angle $(0\bar{1}0) \wedge (1\bar{2}0)$. Average of five measurements, 30° 24′.
Angle $(100) \wedge (1\bar{2}0)$. Average of three measurements, 66° 10′.

From the figures representing the inclinations of the three pinacoids, the following values were calculated[1] for the inclinations of the axes:

---

[1] The writer desires to acknowledge his indebtedness to Dr. A. S. Eakle, of the Department of Mineralogy, for assistance in making the calculations.

$$\alpha = 112^\circ\ 13', \beta = 92^\circ\ 12', \gamma = 94^\circ\ 33'.$$

From the inclinations of the two dome faces (d and e of the figures) on the base, the following values for the axial ratios were obtained:

$$a = 0.8353, b = 1, c = 1.0138.$$

From the intersection of the face m on the brachy- and macropinacoids, the intersection of that plane on the a and b axes respectively, was found to be 1.757; 1, hence its formula is (120). It was observed only when truncating the more acute of the two prismatic angles formed by the intersection of the macro- and brachy-diagonal sections. The macrodome face was present only when of the form $(10\bar{1})$. The brachydome face of the form $(0\bar{1}1)$ was the one usually present, though the form (011) was observed in two instances. Some of the more common combinations are shown in the accompanying figures in which $a = (100)$, $b = (010)$, $c = (001)$, $d = (01\bar{1})$, $e = (10\bar{1})$, $f = (011)$, $m = (\bar{1}20)$.

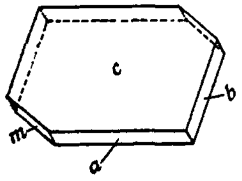

Fig. 1.

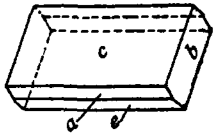

Fig. 2.

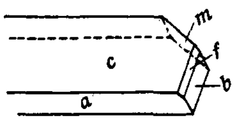

Fig. 3.

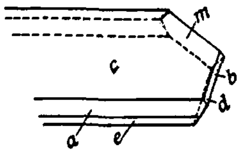

Fig. 4.

FORMULA OF CEROPTENE.

In order to obtain satisfactory material for the quantitative examination, very careful preparation was found to be necessary, since the crystals tend to retain very tenaciously small amounts of the waxy constituents of the secretion. Failure to discover this fact led to an erroneous determination of the formula in the first work on the subject. Of the results recorded below, No. 1 represents materials recrystallized three times from ether, after the preliminary purification, Nos. 2 and 3 were obtained similarly by three recrystallizations from benzene and Nos. 4 and 5 by three recrystallizations from absolute alcohol.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon.............	72.26	72.42	72.62	72.62	72.51	72.48
Hydrogen..........	6.37	6.16	6.13	6.16	6.20	6.20

These figures indicate that the formula of the compound is $(C_9H_9O_2)_n$, the theory for which is $C = 72.44$, $H = 6.09$.

The molecular weight was determined by the freezing-point method, using the usual form of Beckmann apparatus. The results obtained were: With benzene as a solvent, 253, 264, 255; with glacial acetic acid as a solvent, 268, 280: with phenol as a solvent, 259.

The correct formula of the compound then must be $C_{18}H_{18}O_4$ (molecular weight = 298), the low results obtained being probably due to a slight amount of dissociation.

REACTIONS OF CEROPTENE.

The compound possesses decided acid properties. It is dissolved readily by even dilute solutions of the alkaline hydroxides, and these solutions remove it rapidly from a benzene solution of the compound. Long-continued treatment with hot solutions of sodium or barium carbonate or borax dissolve it to some extent. In spite of these facts, it is a difficult matter to prepare the pure salts, owing to their unstability.

If a solution of ceroptene in an alkaline hydroxide is gradually concentrated, oily, yellowish-brown drops finally appear in the bottom of the vessel; these solidify, on cooling, with the formation of a hard, yellow mass, which is easily soluble in water. If some of this solid yellow mass is dissolved and the solution thus obtained is allowed to evaporate spontaneously, the ceroptene gradually separates out in the form of granular masses and the residual solution becomes alkaline. Dilution of alkaline solutions of ceroptene does not bring about precipitation, but neutralization results in the formation of a light yellow precipitate, and, when this is dissolved in benzene, ceroptene crystals of the usual form are produced on evaporation. All the alkaline solutions possess a much more intense color than solutions of the corresponding concentration in organic solvents. Two samples of the potassium salt, prepared with the use of the smallest possible excess of the alkali and separated as solid yellow masses, gave 11.94 and 11.42 per cent. of potassium, respectively. A salt corresponding to the composition $C_{18}H_{17}KO_4$ should contain 11.64 per cent.

The barium salt was prepared by boiling ceroptene with a slight excess of barium hydroxide, filtering the hot solution into a flask previously filled with hydrogen, and allowing to stand. After several days, there appeared a beautifully crystalline salt of a deep yellow color. It is but slightly soluble in water and, on heating, decomposes before reaching a definite melting-point. Determination of the per cent. of barium in two preparations of the salt gave 17.92 and 17.79 per cent., respectively. These figures would indicate a compound corresponding to the formula $(C_{18}H_{17}O_4)_2Ba.2H_2O$, which should contain 17.87 per cent. of barium and 4.69 per cent. of water of crystallization. Experiments in heating the salt showed no appreciable loss up to a temperature of 120°, but at 160° the salt lost 5.23 per cent. in weight and there was some evidence of decomposition.

The silver and lead salts may be obtained by the addition of the nitrates of these metals to solutions of the potassium salt. As thus obtained, they consist of gray, amorphous precipitates which are difficultly soluble. Determination of the silver in a sample of this salt (probably contaminated with small amounts of silver oxide) gave 27.62 per cent. of silver, whereas the anhydrous salt should contain 26.66 per cent.

Attempts to acetylize ceroptene, using glacial acetic acid as a solvent and various combinations of acetic anhydride, acetyl chloride and sodium acetate were entirely unsuccessful. Either the original compound was obtained unchanged, or tarry decomposition products only were produced. Similarly, treatment with benzoyl chloride failed to give any evidence of a definite reaction. With bromine in a chloroform solution, ceroptene liberates at once hydrobromic acid, but the other products of the reaction are non-crystalline and could not be purified. With "Hübl's mixture," using the usual method for the determination of the iodine absorption, no absorption of iodine was shown.

Phenylhydrazine and hydroxylamine do not react with ceroptene under the conditions which usually bring about reactions with aldehydes or ketones, and no bisulphite compound could be prepared. No indications of reducing properties could be obtained by the use of the usual reagents, *i. e.*, alcoholic silver nitrate, Fehling's solution, etc.

Oxidizing agents, dilute nitric acid or potassium permanganate or bichromate in alkaline solution, added to ceroptene and heated, at once give a pronounced odor of benzaldehyde. When 0.5 gram of ceroptene was heated with potassium permanganate for an hour, filtered from the precipitate of manganese dioxide which is formed, acidified and extracted with ether, a white crystalline compound was obtained. This, after purification by recrystallization, was found to melt at 122°, and was sublimed without change. When it was dissolved in absolute alcohol, the solution saturated with dry hydrochloric acid gas, and the whole poured into cold water, oily drops having the characteristic odor of ethyl benzoate separated out. Some carbon dioxide is produced during the oxidation, but it is evident that the chief product of the reaction is benzoic acid, though it is probable that the corresponding aldehyde is first produced.

The treatment of a glacial acetic acid solution of ceroptene with concentrated aqueous hydriodic acid at a temperature of 60° or above, produces a crystalline iodo-compound, which melts at 182°. This appears in crystalline form on cooling the hot mixture, and continues to separate from the solution during several days. The yield obtained in six different preparations ranged from 131 to 145 per cent. of the ceroptene used. Many attempts were made to separate other products of the reaction from the acid mixture, but in every case only tarry compounds, which in solubility, etc., seemed to be identical with the crystalline iodo-compound, were obtained. Iodine is not liberated during the reaction, nor was any considerable amount of the free iodine, which was present in the hydriodic acid used, taken up. The reaction does not take place when other solvents are substituted for the acetic acid, nor does an analogous reaction take place when hydrochloric or hydrobromic acids are used in place of hydriodic acid.

THE IODO-COMPOUND.

The crystals are needle-shaped, often an inch long, with blunt terminations, but the faces are too imperfect to admit of crystallographic study. By transmitted light they are red-brown, but by reflected light they are dark purple. On heating, they first melt with the liberation of iodine, then carbonize, and finally burn without residue. They are insoluble in water, carbon bisulphide and petroleum ether, only slightly soluble in glacial acetic acid, benzene and nitrobenzene, but readily so in alcohol and acetone. It is, however, almost impossible to recrystallize the compound from any of these solvents; when dissolved in alcohol or acetone, the solution leaves, on evaporation, a black, tarry mass which seems to possess all the chemical properties of the original crystals. If acetic acid is added to the acetone solution, a very small amount of the compound separates in crystalline form, the remainder as an amorphous mass. The composition of the compound is shown in the following analyses, each of which represents a different preparation, obtained by washing the crystals, which separated out with glacial acetic acid, and drying at 110°. The iodine was determined by the Carius method, but most of the determinations are somewhat high, owing to the presence of minute particles of glass which could not be separated from the precipitate.

	(1)	(2)	(3)	(4)	(5)	Average.
Carbon	41.26	41.20	41.34	41.07	41.22	41.22
Hydrogen	....	3.44	3.43	3.44	3.41	3.43
Iodine	....	40.25	40.84	40.69	....	40.59

These figures correspond most nearly to the composition $C_{11}H_{11}IO_3$, the theory for which is $C = 41.51$, $H = 3.46$, $I = 39.94$.

The molecular weight was determined with approximate accuracy only; the small amount of material available necessitated the use of freezing-point methods and the very slight solubility, in the solvents commonly employed, introduced a large percentage error in these determinations. Using nitrobenzene as a solvent, two approximate results, 310 and 357 respectively, were obtained. The theory for $C_{11}H_{11}IO_3$ is 318. These results are sufficient to establish the formula of the compound as written above.

REACTIONS OF THE IODO-COMPOUND.

The iodo-compound shows acid properties similar to those of ceroptene, but the preparation of the pure salts is attended with many difficulties. The salts are characterized by red or brown colors and possess weak dyeing properties with woolen goods. An approximately pure potassium salt yielded 15.27 per cent. of potassium; the compound $C_{11}H_{11}KO_4$ should contain 15.89 per cent. If an alkaline solution of the iodo-compound is acidified, there is produced a yellow precipitate which coagulates to form resinous masses. It is soluble in alcohol, acetone, chloroform and glacial acetic acid, but it can not be crystallized from any of these solvents or combinations of them. It does not contain iodine and melts very indefinitely at 52°. Owing to its amorphous nature and the difficulty of drying without effecting decomposition, an accurate determination of its formula could not be made. The result of three combustions and a single molecular weight determination indicate that the formula is $C_{11}H_{12}O_4$.

On oxidizing the iodo-compound with nitric acid or potassium permanganate, as in the treatment of ceroptene, similar evidence for the formation of benzaldehyde and benzoic and carbonic acids was obtained. With the usual reagents for the detection of aldehyde or ketone groups, no evidence of any reaction could be obtained. Attempts to reduce with sodium amalgam and also with metallic magnesium led to the formation of compounds which could not be purified.

The exact nature of the reaction involved in the formation of the iodo-compound is still a mystery. Apparently, it is the only product of that reaction. If it be assumed that 1 molecule of ceroptene produces 1 molecule of the iodo-compound, the theoretical yield should be 106.7 per cent. Since the actual yield varies from 131 to 145 per cent. and since a large amount of a non-crystalline compound, which seems to be identical with the crystalline product, is produced at the same time, it is probable that 2 molecules of the iodo-compound are produced from 1 of ceroptene. Evidently the acetic acid takes part in the reaction, as is also evinced by the failure to obtain the compound when other solvents are used. Further, this involves more than the simple addition of an acetyl group, since no evidence of acetic acid nor of any volatile compound could be obtained on saponifying, acidifying the product, and distilling. As to the structure of the iodo-compound, it can only be said at present that it contains a single benzene nucleus with a side chain, and that, since the iodine is easily displaced, it is not a part of a second ring, though as the substance does not add iodine, and hence contains no ethylene groupings, it is somewhat difficult to write a structural formula in which the ring structure is absent. At first sight it would seem as though the quantitative relation involved in the formation of the iodo-compound would indicate that ceroptene was composed of two symmetrical groups, each containing a single benzene nucleus, which is split by the hydriodic acid. If this were strictly so, however, the formation of dibasic as well as monobasic salts should be expected. Any attempt to express the probable structure of either compound is at present unprofitable.

IDENTIFICATION OF CEROTIC ACID.

If the waxy portion of the secretion, which remains after the separation of the ceroptene, is digested with hot alcohol, filtered while hot, and allowed to cool, a white amorphous precipitate separates out. This precipitate fused at 64° and, on cooling, formed a hard, brittle mass. By two further precipitations from alcohol, a product was obtained which melted at 70°. A more rapid method of separating the same substance was to digest the wax with a dilute solution of an alkaline hydroxide and treat the undissolved portion with alcohol as in the other method. When obtained by either process, the product was of a greenish color after fusion, was readily soluble in petroleum ether, acetone and ethyl ether, and was precipitated from the solution by lead acetate. The alcoholic solution shows only faint acid properties, and the amount of potassium hydroxide necessary to react with 1 gram, determined by the ordinary process for saponification number, was found to be 0.22 gram. The combustion of three different preparations gave the following results:

	(1)	(2)	(3)	Theory for $C_{27}H_{24}O_2$.
Carbon	79.04	78.29	80.24	78.94
Hydrogen	12.32	12.56	13.30	13.26

A single determination of the molecular weight by the freezing-point method, using benzene as the solvent, gave 482, though the percentage error involved in this determination is comparatively large, owing to the very slight solubility in this solvent. In all the particulars noted above, the substance agrees so closely with the substance originally separated by Brodie from beeswax that there can be little doubt that it is essentially cerotic acid. The preparations thus far obtained are impure.

THE OTHER CONSTITUENTS OF THE SECRETION.

As noted earlier in this paper, a second crystalline compound is obtained from the tarry precipitate produced by acidifying the alkaline solution of the secretion. Treatment of this precipitate with alcohol leaves a small amount of ceroptene, together with the substance just referred to. It is a difficult matter to separate it from the ceroptene, but a long series of fractional crystallizations from acetone finally separated it in pure condition. It forms brown, monoclinic prisms which melt at 185°. Some of these were obtained large enough for crystallographic study. The only forms present were the prism, basal plane and clinopinacoid. The angles measured were as follows:

$(110) > (1\bar{1}0)$ (average of 9 measurements) $= 77° 32'$
$(110) > (001)$ " " 4 " $= 57° 31'$
$(010) > (001)$ (result of a single measurement) $= 89° 34'$.

Barely enough of the pure substance was obtained for a single combustion, the results of which were C = 69.01 per cent., H = 4.95 per cent.

That portion of the acid precipitate which is easily soluble in cold alcohol, and which forms nearly one-half the total secretion, is of an entirely amorphous nature. In a long series of experiments with a great variety of solvents, only brown, sticky compounds were obtained. The compounds of which this material is composed are evidently strongly acid in character, and their lead salts are insoluble. Combustions of several samples of the substance gave results varying from 57.76 to 68.33 per cent. of carbon, and from 7 to 7.17 per cent. of hydrogen. The material is clearly a mixture of several acids.

CHEMICAL LABORATORY, UNIVERSITY OF
CALIFORNIA, August 15, 1903.